



Research paper

Use of aligned triphenylamine-based radicals in a porous framework for promoting photocatalysis



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ABSTRACT

The Ca-MOF **FIR-29** is synthesized and exhibits a honeycomb lattice of hexagonal channels with an aperture of ~ 16 Å, giving a BET surface area of $2061 \text{ m}^2 \text{ g}^{-1}$. The consecutive slipped π – π stacking interactions of photoactive tris((4-carboxyl)phenyl)durylamine (TCPA) groups on the surface of hexagonal channels makes it an effective photocatalyst for catalyzing the typical Mannich photocatalysis, forming β -tetrahydroisoquinoline ketones in high isolated yields. Catalytic activity for **FIR-29** is about 2.7 times enhancement over that for mesoporous DUT-63 consisted of discrete TCPA groups without any intermolecular interaction. This is mainly due to the fact that the rigid compact stacking of tri([1,1'-biphenyl]-4-yl)amine (TBPA) is conducive to form stable TBPA radical, and is optimal for electron or energy transfer to expedite the reactivity of sp^3 carbon atoms and allow higher photocatalytic conversion.

Dedicated to professor Xin[HYPHEN]Tao Wu on the occasion of his 80th

1. Introduction

In the past decades, visible-light-driven photocatalysis as an eco-friendly and energy-efficient method for organic synthesis has been extensively explored [1–6]. Compared with traditional noble metal photocatalysts, organic dyes have recently attracted much attention of synthetic chemists because their promising characteristics of efficient visible-light absorption, enhanced stability, and modification susceptibility promote their application in photocatalysis [7–14]. For example, triphenylamine (TPA) and its derivatives have excellent hole-transport properties and have been widely used to construct hole-transport materials for efficient photoredox reactions [15,16]. However, the homogeneous catalysis of these TPA-based complexes makes their recycling and products separation difficult, which will further delay their practical applications in photocatalytic processes [17]. An effective approach to resolve this issue centers is to trap these TPA-based complexes into porous solid materials, making easy catalysts reuse and products purification [18–23].

Metal-organic frameworks (MOFs) are interesting hybrid solids with ordered infinite networks consisting of organic bridging ligands and inorganic nodes [24–32]. The unique porous structure of MOFs encapsulating photoactive organic groups allows them to demonstrate considerable promise in photocatalysis [26,33–42]. Recently, to overcome the current limitation of visible-light-driven photocatalysis and

enhance photocatalytic conversion of poorly active chemical bonds in organic synthesis, a significant consecutive photoinduced electron transfer (conPET) process [43] of the perylene diimide (PDI) radical anion was applied to a Zn-PDI MOF for the reduction of aryl halides [33]. Although TPA derivatives can't perform such conPET process similar to PDI units, long-range π – π stacking of TPA derivatives with conjugated systems, such as tri([1,1'-biphenyl]-4-yl)amine (TBPA), can support some favorable factors for photocatalysis, including 1) the formation of stable radical with high local concentration; 2) a strong attraction to aromatic substrate molecules; 3) their packing state being optimal for electron or energy transfer [33]. These favorable factors endow desirable photocatalysis potential of TPA derivatives. Especially, the incorporation of well-organized TBPA fragments into MOFs represents a promising approach to heterogenize these photoconversions and to overcome the restrictions of the homogeneous process. Tris((4-carboxyl)phenyl)durylamine (H_3TCPA), a trigonal ligand that contains the photoactive TBPA group, has been employed to build some MOFs used for their gas sorption and optical properties [44–48], but none of them shows visible-light-driven photocatalysis in organic synthesis, because the TBPA units in these MOFs were not aligned appropriately.

In this paper, the redox-active Ca-MOF, $\{[\text{Ca}_5(\text{TCPA})_3(\text{H}_2\text{O})_6]^+\}_n\text{nNO}_3^-$, **FIR-29**, FIR denotes Fujian Institute of Research) shows hexagonal channels with an aperture of 16 Å and well-organized aggregation of photoactive TBPA moieties as aryl radicals, making it an effective photocatalyst. The typical oxidative Mannich reaction [49] of *N*-phenyltetrahydroisoquinoline and

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nonactivated ketones under mild conditions is selected as model substrates to examine the feasibility of the optimal photoinduced electron transfer (PET) process in the consecutive long-range $\pi\cdots\pi$ stacking of the stable TBPA radicals.

2. Experimental

2.1. Materials and methods

Commercially available reagents were used as received. Thermal gravimetric analysis data were obtained with an NETZSCH STA 449C analyzer. All samples and reference (Al_2O_3) were enclosed in a platinum crucible and were heated from 25 to 700 °C at a rate of 10 °C/min under an N_2 atmosphere. X-ray powder diffraction (XRPD) patterns were collected on a Rigaku Mini 600 X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at a scanning rate of 5°/min for 2θ ranging from 4° to 40°. Simulated XRPD patterns were calculated using Mercury from corresponding single-crystal structural models. ^1H NMR spectra were recorded on a Bruker Avance 400 (400.1 MHz for ^1H NMR). The deuterated solvents used are indicated in the experimental part. EPR spectra were recorded on a Bruker BioSpin E500 EPR spectrometer with a 100 kHz magnetic field modulation at room temperature equipped with a 16 mW ultraviolet lamp. Gas adsorption measurement was performed in the ASAP 2020 System. Optical diffuse reflectance spectra were measured at room temperature on a Perkin Elmer Lambda-950 UV/Vis/NIR spectrophotometer by using BaSO_4 as baseline sample.

2.2. Preparation of $\{[\text{Ca}_5(\text{TCPA})_3(\text{H}_2\text{O})_6]^{+}\}_n\text{NO}_3^{-}$ (FIR-29)

H_3TCPA (60 mg), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (50 mg), 4 mL dimethylacetamide (DMA) and 0.5 mL H_2O in an 8 mL vial was stirred for 30 min, and then sealed and heated in an oven at 120 °C for 3 days. The vial was then cooled to room temperature. After washing with fresh DMA, yellow triangular-prism-shaped crystals were obtained in pure form (Yield: 70 mg, 57% based on H_3TCPA).

2.3. X-ray crystallography

The diffraction data of **FIR-29** was collected on a SuperNova diffractometer equipped with a copper micro-focus X-ray sources ($\lambda = 1.5406 \text{ \AA}$) and an Atlas CCD detector under 100 K. Empirical absorption correction used spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The structure was solved by direct methods and refined with full-matrix least-squares technique using *SHELXL-2014*. All non-hydrogen atoms were refined with anisotropic displacement parameters. The diffused electron densities resulting from these residual solvent molecules were removed from the dataset using the *SQUEEZE* routine of *PLATON* and refined further using the data generated. The contents of the solvent region are not represented in the unit cell contents in the crystal data. Crystal data of **FIR-29**: $\text{C}_{117}\text{H}_{72}\text{N}_3\text{O}_{24}\text{Ca}_5$, $M_r = 2104.17$, space group $P3_121$, $a = 37.0787(5) \text{ \AA}$, $c = 30.0922(7) \text{ \AA}$, $V = 35828.9(13) \text{ \AA}^3$, $Z = 6$, $D_c = 0.585 \text{ g cm}^{-3}$, $F_{000} = 6522$, CuK α radiation, $\lambda = 1.54184 \text{ \AA}$, $T = 100.0(2) \text{ K}$, 48768 reflections collected, 29178 unique ($R_{\text{int}} = 0.0757$). Final GooF = 1.095, $R1 = 0.0894$, $wR2 = 0.2211$, R indices based on 6522 reflections with ($I > 2\sigma(I)$) (refinement on F^2).

2.4. Typical experimental procedure for catalysis

Representative procedure: to a 10 mL Schleck flask equipped, crystalline powder of **FIR-29** (5.0 mmol% based on Ca_5 cluster), the respective substrate (0.5 mmol) and L-proline (6 mg) were added into dry MeCN (3 mL) and acetone (1 mL) via stirring. Then the reaction mixture was stirred under open air for 8 h at a distance of about 5 cm from a 7 W blue LEDs lamp. Upon the completion of reaction, as monitored by TLC (petroleum ether: ethyl acetate = 4:1), the crude

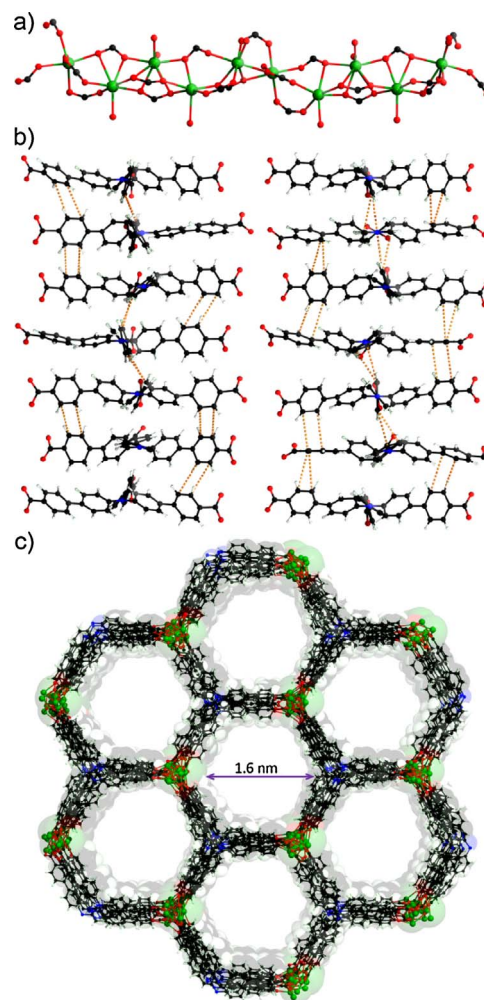


Fig. 1. (a) A Ca-COO chain running along the c axis; (b) Two parallel stacking arrays of TCPA fragments; (c) 3D framework showing nanoporous hexagonal channels.

reaction mixture was purified by flash chromatography on silica gel (silica: 200–300 mesh; eluent: petroleum ether/ethyl acetate (4:1) to provide the corresponding pure product.

3. Results and discussion

3.1. Crystal structure

The reaction of H_3TCPA and $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in a mixed DMA/ H_2O solvent at 120 °C for 3 days afforded the yellow triangular-prism-shaped crystals of **FIR-29**. Single-crystal X-ray diffraction analysis reveals that **FIR-29** crystallizes in a chiral space group $P3_121$. In each asymmetric unit, the five independent Ca^{2+} ions with the 6-, 7- or 8-coordinated geometries (Fig. 1a) are bridged by carboxyl groups to form a metallic pentamer $\text{Ca}_5(\text{COO})_9$ and are further linked by three carboxyl groups in an ABBA... arrangement, giving rise to an infinitely positive Ca-COO chain along the c axis. The TCPA ligands around the Ca-COO chain are closely arranged along the c direction, showing intermolecular interactions of consecutive long-range slipped $\pi\cdots\pi$ stacking with the distance between two C atoms from the phenyl rings of TCPA ligands measured at 3.5–3.8 Å (Fig. 1b) [50]. The favorable factor may support optimal electron or energy transfer process and endow desirable photocatalysis potential of **FIR-29**. In the structure of **FIR-29**, each rod-like Ca-COO chain is then connected to other six chains by long trigonal bridging ligand TCPA to form a 3D rod-packing architecture (Fig. 1c). Such rod-and-spacer approach has been proved

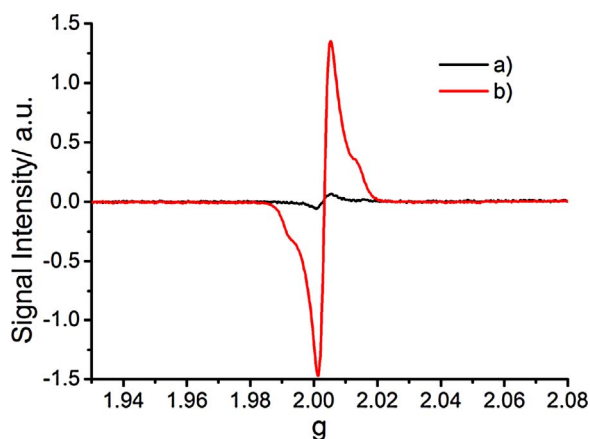


Fig. 2. EPR spectra of K_3TCPA (a), and $FIR-29a$ (b).

to be one of the most effective methods to obtain porous metal-carboxylate structures because of the absence of interpenetration [51–53]. Furthermore, this open framework of **FIR-29** exhibits a honeycomb lattice of hexagonal channels along the c axis, and the aperture for each hexagonal channel is approximately 16 Å (including van der Waals radii). The solvent-accessible volume (including charge-balancing anions) of **FIR-29** is about 67.1% of the total crystal volume estimated by the *PLATON* program [54]. The free spaces are occupied by the disordered solvent molecules and charge-balancing anions.

3.2. TGA, EPR and UV/Vis spectrum

The phase purity of **FIR-29** is testified by powder X-ray diffraction (PXRD) (Fig. S2b). The Thermogravimetric analysis (TGA) curve of **FIR-29** reveals a weight loss of 40.1% under 200 °C, corresponding to the release of guest molecules (Fig. S1). **FIR-29** was soaked in MeCN solution for 3 days and then activated under high vacuum at 150 °C for 8 h, forming the hollow phase **FIR-29a**. The electron paramagnetic resonance (EPR) spectrum (Fig. 2) of **FIR-29a** (28.9 mg, 0.04 mmol TCPA) shows a peak at $g = 2.003$, indicating that the nitrogen atoms of the organic TBPA species incorporated in the host solid of **FIR-29a** have been oxidized to free radicals and show much higher signal intensity after irradiation of blue LEDs for 60 min, which is about 19 times enhancement over that for K_3TCPA (28.8 mg, 0.04 mmol TCPA) under the same conditions. Slipped π stacking interactions between TCPA ligands supports their excellent ability to delocalize and migrate excitons, which in turn supports the formation of stable TBPA radical anions in the host compound. The UV/Vis spectrum of **FIR-29** shows a strong absorption band at 416 nm, maybe corresponding to the $n-\pi^*$ and $\pi-\pi^*$ transition of TCPA ligands (Fig. S3). The band gap energy of **FIR-29** determined from Kubelka–Munk function is 2.58 eV.

3.3. Gas sorption

To examine the permanent porosity of **FIR-29**, the gas sorption of the desolvated form (**FIR-29a**) was studied. The N_2 sorption isotherms at 77 K reveal an N_2 uptake of $681 \text{ cm}^3 \text{ g}^{-1}$ at 1 bar, giving a BET surface area of $2061 \text{ m}^2 \text{ g}^{-1}$ and a micropore volume of $1.05 \text{ cm}^3 \text{ g}^{-1}$ (Fig. 3). A pore size distribution analysis by non-localized density functional theory (NLDFT) methods utilizing N_2 gas at 77 K shows a broad distribution of 1.0–1.8 nm (Fig. S4). Clearly, the pore size of 1.6 nm takes advantage of numbers in **FIR-29a**. Such excellent sorption property is due to the $\pi-\pi$ interaction between TCPA ligands, which is beneficial to stabilize the honeycomb channels in **FIR-29**.

3.4. Mannich reaction of *N*-phenyltetrahydroisoquinolines with acetone

Tris(4-bromophenyl)aminium hexachloroantimonate, as a well-

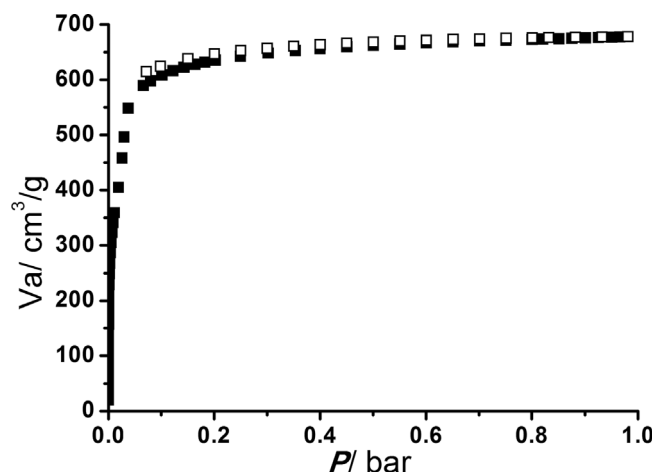
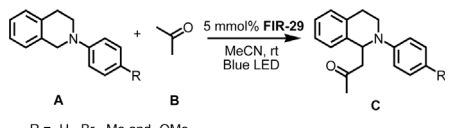


Fig. 3. Gas sorption isotherms of N_2 at 77 K for **FIR-29a**.

known stable radical cation salt, was demonstrated to be an efficient initiator for the oxidative Mannich reaction of tertiary amines and nonactivated ketones under mild neutral conditions [55]. The organized aggregation of TBPA groups in **FIR-29** creates stable free radicals and also leaves considerable space for the ingress and egress of fitted substrates and products, leading to its potential application of photocatalysis in an oxidative Mannich reaction catalyzed by free radicals. By using MOF **FIR-29** as visible light photocatalysts under mild reaction conditions, we become interested in investigating the PET process of aligned TBPA radicals by using the typical Mannich-type reaction of *N*-phenyltetrahydroisoquinoline (**A**) with acetone (**B**), and L-proline (to form the enamine nucleophile) as a probe reaction, which involves the activation of sp^3 carbon atoms and the formation of C–C bonds [56]. 5 mmol% (based on Ca_5 cluster) photocatalyst **FIR-29** was used as a heterogeneous photocatalyst for the above aerobic Mannich-type reaction of under irradiation of blue LEDs at ambient conditions for 8 h. As can be seen in Entries 1–3 of Table 1, the controlling experiments show that each component, including light, oxygen and the MOF photocatalyst, is necessary for the reaction. Once these conditions were met, formation of the desired cross-coupling product (**C**) in good yield was observed (Entry 8). The β -tetrahydroisoquinoline ketone (**C**), the principal product was confirmed by 1H NMR spectroscopy (See Supplementary Information). For photocatalyst **FIR-29**, the isolated yield of the reaction is 85% after 8 h, which is much higher than that (46%) of K_3TCPA (Entry 4). An explanation for this behavior may be that the rigid compact stacking of TBPA is conducive to optimal electron or energy transfer pathway during the PET process of the TBPA radical expediting the functionalization of the sp^3 C–H bond adjacent to a nitrogen atom in **A** and allowing higher photocatalytic conversion. Additionally, the extended conjugated system in **FIR-29** endows on TBPA exceptional optical stability in combination with strong visible-light absorption, both conditions which are favourable for the application of this heterogeneous process [33]. In order to deeply understand significance of such PET process in the long-range $\pi-\pi$ stacking of the stable TBPA radicals for the Mannich reaction, a mesoporous MOF (DUT-63) [57], in which the Cu paddle-wheel units are linked by discrete TCPA ligands without any intermolecular interaction (Such as, H-bond and $\pi-\pi$ interactions) (Fig. S5 and S6), is also employed to perform the same Mannich reaction. As expected, the isolated yield of 32% (Entry 5) is very low and even lower than that of K_3TCPA , because the energy conferred by discrete TBPA radicals may be inefficient to convert the sp^3 C–H bond. [33]. Some MOFs have achieved considerable success in this field, however costly and toxic metal reagents often act as catalysts. For example, Sn-mediated MOF (UNLFP-12) and UiO-68-Se achieved a yield of 98% and 94% for the aerobic Mannich reaction of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline with acetone under air [56,58]. Au^{3+}

Table 1

The visible light induced Mannich reactions of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline (A) with acetone (B).

			
Entry	Conditions	Substituent	Yield/% ^a
1 ^b	no catalyst	-R = -H	trace
2 ^c	no light	-R = -H	trace
3 ^d	no oxygen	-R = -H	trace
4 ^e	K ₃ TCPA	-R = -H	46
5 ^f	DUT-63	-R = -H	32
6 ^g	Eosin B	-R = -H	42
7 ^h	Eosin Y	-R = -H	40
8 ⁱ	FIR-29	-R = -H	85
9 ^j	FIR-29	-R = -H	36
10 ^k	FIR-29	-R = -H	36
11 ^l	FIR-29	-R = -H	83
12 ^m	FIR-29	-R = -H	82
13	FIR-29	-R = -Br	88
14	FIR-29	-R = -Me	81
15	FIR-29	-R = -OMe	89

^a Yield of the isolated products.

^b The reaction without any catalyst.

^c The reaction in the presence of **FIR-29** was stirred under the dark and air atmosphere.

^d The reaction mixture was strictly degassed and then irradiated under an Ar atmosphere.

^e 15 mmol% K₃TCPA.

^f 15 mmol% (based on TCPA³ ligand) DUT-63.

^g 15 mmol% Eosin B used as a photocatalyst.

^h 15 mmol% Eosin Y used as a photocatalyst.

ⁱ Run 1.

^j Yield after 3 h.

^k The filtration test by removing the catalyst **FIR-29** after 3 h and continuing the reaction for another 5 h.

^l Run 2.

^m Run 3.

complexes-loading MOF achieved an isolated yield of 84.2% under a solvent-saturated oxygen atmosphere [59]. More importantly, the catalytic activity of **FIR-29** is much higher than two simple dyes, Eosin B and Eosin Y, as homogeneous catalysts (Entries 6–7), and bears comparison with the reported PDMS-RB sponge photocatalyst by anchoring Rose Bengal dye [60]. As a green photocatalyst without costly and toxic metal, **FIR-29** shows comparable catalytic activity to aforementioned MOFs and promotes photocatalysis via the optimal PET process of well-organized ligands rather than metal reagents.

The heterogeneity of photocatalyst **FIR-29** was confirmed by removal of the catalyst after 3 h (yield: 36%), which resulted in essentially no further production of the final product C, showing that the heterogeneous photocatalyst **FIR-29** fails to attract any catalytically active species into the reaction system (Entries 9–10). The reusability of the photocatalyst **FIR-29** was also investigated by using the same batch of **FIR-29** for three successive catalytic cycles of this reaction. The results indicate that catalytic activity of **FIR-29** remains fairly consistent after three cycles (yields: $\geq 82\%$) (Entries 11–12). XRPD measurements of the recycled photocatalyst revealed maintenance of its crystalline structure, confirming the stability of **FIR-29** in the catalytic system (Fig. S2c). We further extended the scope of this aerobic Mannich reaction catalyzed by the photocatalyst **FIR-29** (Table 1) and observed that A with various substituent groups could be coupled with acetone readily to afford the desired products in good to excellent yields (Entries 13–15). It's worth noting that *N*-phenyl-tetrahydroisoquinoline derivatives with electron-donating and electron-withdrawing groups on the phenyl rings are all compatible in the aerobic C–C coupling reaction.

Previous research indicated $O_2^{\cdot-}$ was the active intermediate

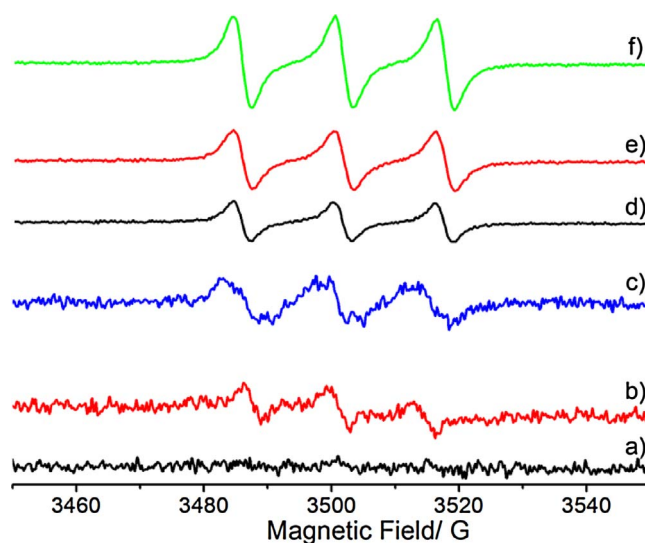
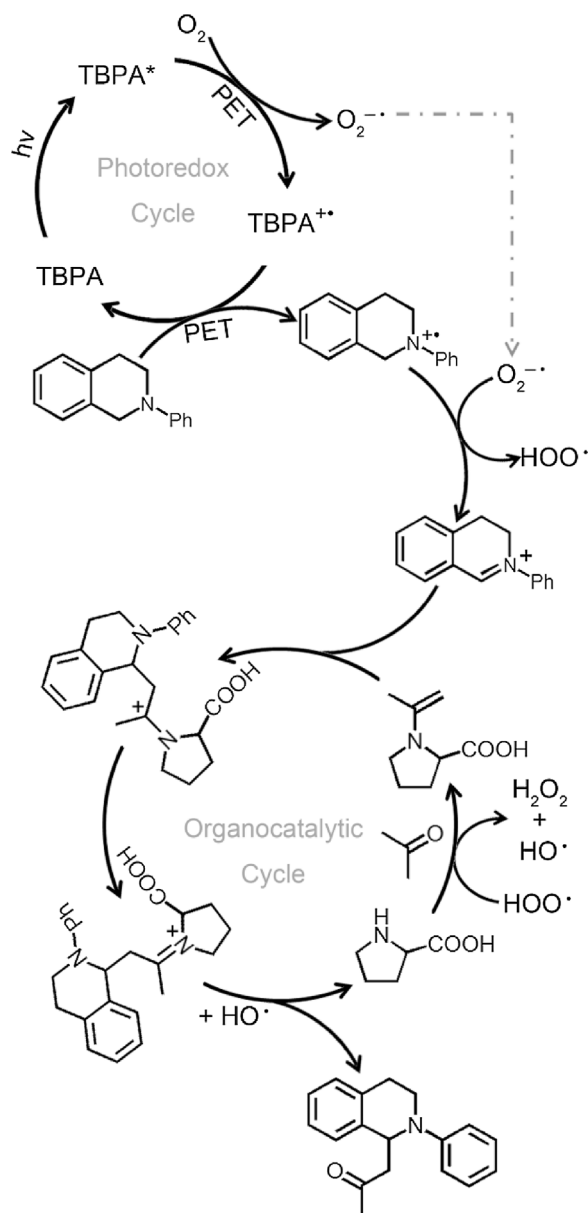


Fig. 4. EPR spectra of the CH₃CN solution with DMPO (a); **FIR-29** and DMPO (b); **FIR-29**, A, and DMPO (c) under irradiation of blue LEDs for 60 min. EPR spectra of the CH₃CN solution with TEMP (a); **FIR-29** and TEMP (b); **FIR-29**, A and TEMP (c) under irradiation of blue LEDs for 20 min (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

species in the visible-light-driven aerobic CDC reaction [8,58,61–63]. To understand the photocatalytic process of **FIR-29** in detail, the EPR measurements are conducted in 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP), which are used to capture superoxide radical anion $O_2^{\cdot-}$ and singlet oxygen 1O_2 , respectively. As shown in Fig. 4, upon irradiation of the CH₃CN mixture of **FIR-29** and DMPO in the air, the formation of $O_2^{\cdot-}$ under the reaction conditions is confirmed by EPR spectroscopy (Fig. 4c). As shown in Fig. 4d–e, no 1O_2 can be generated during the photocatalysis process. These findings indicate that $O_2^{\cdot-}$ is the active intermediate species in the reaction. Mechanistically, we proposed that the highly reactive iminium intermediate was formed by the oxidation of the C–H bond adjacent to the nitrogen of A (Scheme 1). The TBPA array in **FIR-29** accepts a number of photons from the visible light source to form the excited state TBPA* array and then is immediately quenched by oxygen via a PET process, generating the array of radical TBPA^{•+} cations and the superoxide radical anion $O_2^{\cdot-}$. The array of radical TBPA^{•+} cation accepts electrons from molecule A forming the radical anion A^{•+} and simultaneously reducing TBPA^{•+} to its ground state. These superoxide radical anions $O_2^{\cdot-}$ generated by the photoredox cycle of TBPA may abstract a hydrogen atom from the radical cation A^{•+} to form the desired iminium ion A⁺, which enters the organocatalytic cycle and reacts with the enamine nucleophile generated by L-proline-activated acetone to give the desired product [56].

4. Conclusions

In summary, we have first constructed a noble-metal-free Ca-MOF (**FIR-29**) with organized aggregation of photoactive TBPA groups as aryl radicals. The robust **FIR-29** acts as an efficient and heterogeneous photocatalyst for aerobic Mannich reactions to form β -tetrahydroisoquinoline ketone products under visible light. This reaction depends upon the heterogeneity of photocatalytic transformation, and the synergistic effect of nanopores and a PET process between well-organized TBPA radicals. It is envisioned that combining organic molecular catalysts in MOFs can be an effective approach to optimizing the activity of heterogeneous catalysts for efficient photocatalysis.



Scheme 1. Proposed mechanism of Mannich photocatalysis for **FIR-29**.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.09.054>.

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